THE SEPARATION OF CLAY MINERALS BY CONTINUOUS PARTICLE ELECTROPHORESIS

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Abstract

A Beckman Continuous Particle Electrophoresis System is capable of separating mixtures of kaolinite and montmorillonite into five or more fractions by one pass through the instrument. The lowest and highest mobility fractions obtained from a 50:50 artificial mixture of these clays contain, respectively, 85 percent montmorillonite/15 percent kaolinite, and 5 percent montmorillonite/95 percent kaolinite. The intermediate fractions contain varying proportions of the two minerals. Mixtures of clays in Recent sediments can also be separated, but not as effectively as artificial mixtures. The most complete separation was obtained in a 4×10^{-4}M Na_2CO_3 buffer containing 5 percent ethylene glycol at pH 10.

Electrophoresis has been suggested as a method of separating clay minerals by Sillén[2] and by Beavers and Marshall (1951). It is only recently, however, that suitable equipment has become available (Strickler *et al.*, 1966, Strickler, 1967). The purpose of this study was to find a rapid method for separating clay minerals with a minimum change in chemical and physical properties.

The instrument used was a Beckman Continuous Particle Electrophoresis System. The principle is shown in Figure 1. Cell A contains a free-flowing column of buffer solution approximately 2 mm in thickness, across which a DC potential of up to 100 V/cm is maintained. At the base of the cell the buffer solution exits through a row of tubes, whose outflows are collected separately. The sample suspension is introduced into the top of the cell as a fine stream, and the particles migrate laterally in the electric field as they are carried down by the flowing buffer solution. If two particles have different electrophoretic mobilities they will follow different paths through the cell (1 and 2 in Fig. 1), and will exit by different tubes. The factors which determine the electrophoretic mobility of a particular clay in a particular buffer solution are not completely understood. In general however, differences in lattice charge will result in differences in electrophoretic mobility, and, for the size range normally encountered in the clay fraction of sediments, electrophoretic mobility is independent of particle size.

The buffer solution may be of any desired composition, but should be in the concentration range 10^{-4} to 10^{-3} molar. The clay sample is sus-

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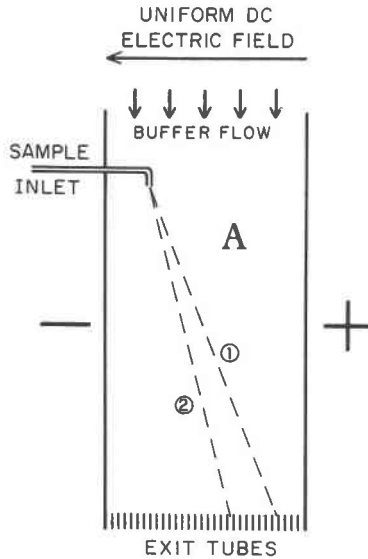[2] Unpublished notes (1966), Library of Scripps Institution of Oceanography, La Jolla, California.

FIG. 1. Principle of the electrophoresis cell.

pended in an identical buffer solution, and should be equilibrated thoroughly with the buffer either by dialysis or by repeated washing. It is essential that the clay disperse completely in the buffer solution, and ultrasonic dispersion is required immediately prior to the electrophoretic separation procedure.

The degree of separation which can be achieved by one pass through the instrument using an artificial mixture of kaolinite (A.P.I. Standard No. 9) and montmorillonite (A.P.I. Standard No. 30) is shown in Figure 2. Numbers 1–5 represent fractions collected from successive exit tubes. Fraction 1 has the lowest mobility. The peak at 7 Å corresponds to kaolinite, and the peak at 17 Å to montmorillonite. It was found that the mobilities of these minerals differed by less than 10 percent in simple buffers. A difference in mobility of at least 10 to 20 percent is required for complete separation. A search was made for buffer additives which would be adsorbed to different extents by different minerals in order to modify their relative mobilities. The substances investigated were: (1) Salts of polyvalent cations: barium acetate, lanthanum chloride. (2) Organic molecules and cations: ethylene glycol, cetyltrimethylammonium chloride, choline chloride. (3) Sodium polymetaphosphate.

The most effective of these was ethylene glycol. A separation performed in a sodium carbonate buffer containing 5 percent ethylene glycol is shown in Figure 2b. The principal difficulty encountered with the selec-
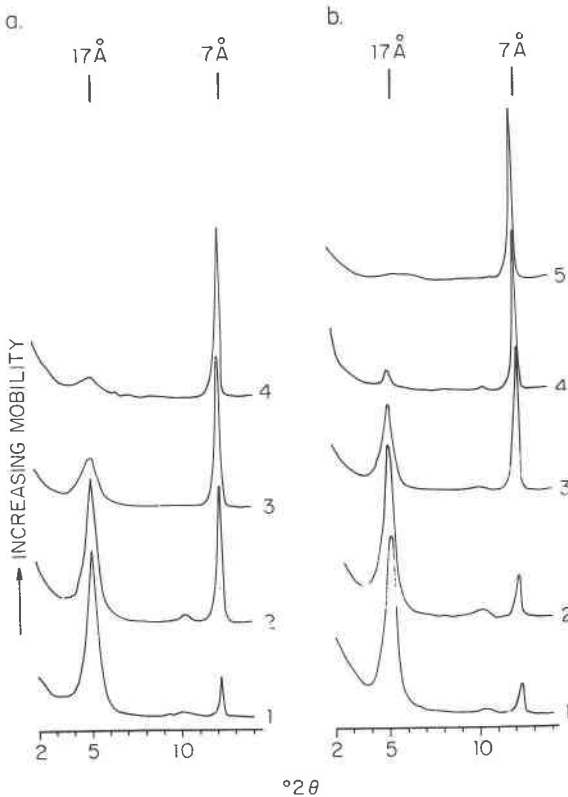
FIG. 2. Smoothed diffractometer traces showing the separation of a mixture
of kaolinite and montmorillonite.

a) without ethylene glycol
b) with 5% ethylene glycol
Buffer: 4×10^{-4}M Na_2CO_3, pH 9.0.
Potential gradient: 100 V/cm, buffer flow: 24 ml/min.

tive adsorption approach was that coagulation generally occurred before
there was any significant reduction in electrophoretic mobility. This is
consistent with previous observations on clay minerals (Marshall, 1964
pp. 339–342). The difference in mobility between kaolinite and mont-
morillonite in the sodium carbonate/ethylene glycol buffer, from mea-
surements on the single clays, is approximately 20 percent. The separa-
tion achieved using a mixture of these clays is less than would be expected
from this difference, which suggests that some particle-particle interac-
tion is reducing the effectiveness of the separation. A second pass of the
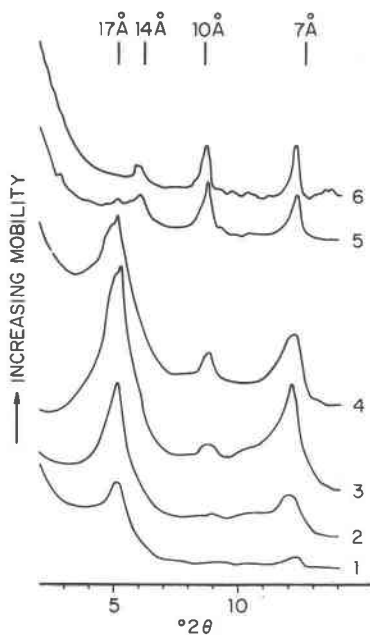fractions through the instrument produces some further separation, but

FIG. 3. Smoothed diffractometer traces showing the separation of a shallow-water marine sediment, No. S-210, $<2\mu m$. Buffer: $4\times10^{-4}M$ $Na_2CO_3/5\%$ ethylene glycol, pH 10.0. Potential gradient: 100 V/cm, buffer flow: 24 ml/min.

the improvement is generally disappointing in terms of the labor involved.

Effectiveness of separation on two Recent marine sediments is shown in Figures 3 and 4. These particular samples were treated with hydrogen peroxide prior to separation, a necessary procedure for samples containing more than approximately a half-percent organic matter. A sample of clay from the Mid-Atlantic Ridge, which contained very little organic matter, showed some separation without hydrogen peroxide treatment. The samples whose separations are indicated in Figures 3 and 4 contained approximately 20 percent amorphous iron oxide and aluminosilicate material, as determined by the methods of Mehra and Jackson (1960) and Hashimoto & Jackson (1960). It was not possible to obtain a separation on sediment from which the amorphous material had been dissolved, possibly because the dissolution procedure results in the deposition of traces of sulfur or iron sulfide on the clay surfaces.

Although pure samples of each mineral cannot be separated from a natural mixture by the present technique, the separations which can be attained may be useful for a number of purposes:

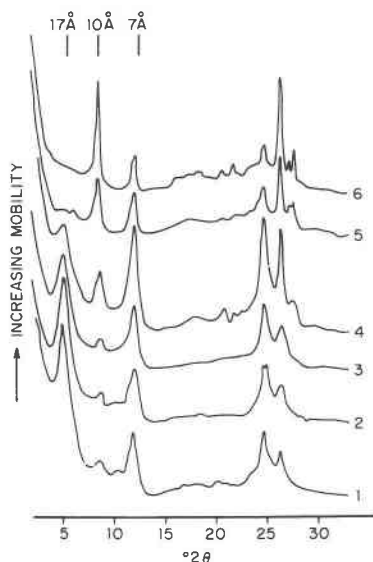1. To reveal the presence of a mineral which is not detectable by X-

FIG. 4. Smoothed diffractometer traces showing the separation of a marine sediment. No. Bon 390 (0–2 cm), <2μm. Buffer: 4×10^{-4}M Na_2CO_3/5% ethylene glycol, pH 10.0, Potential gradient: 100 V/cm, buffer flow: 24 ml/min.

ray diffraction of the bulk sample, such as the nonexpanding 14 Å material in Figure 3.

2. To assign a particular trace element to a particular mineral, using chemical analyses of the separated fractions.

3. To estimate the chemical composition of each mineral, and to determine a weighting factor relating the X-ray peak area of each mineral to its abundance. This procedure depends on chemical and X-ray analysis of the separated fractions. The extent to which it is successful depends very much on the nature of the original clay sample.

The separation based on electrophoretic mobility is somewhat similar to the results which would be expected from a separation based on grain size. This limits the extent to which the two methods can be used in conjunction. It is very probable that the technique will be improved by further development of the selective adsorption technique, and by introduction of instruments with greater stability and higher preparative resolution.

REFERENCES

BEAVERS, A. H., AND C. E. MARSHALL (1951) The cataphoresis of clay minerals and factors affecting their separation. *Soil Sci. Soc. Amer. Proc.*, **15,** 142–145.

HASHIMOTO, I., AND M. L. JACKSON (1960) Rapid dissolution of allophane and kaolinite-halloysite after dehydration. *Clays Clay Minerals, Proc. Nat. Conf.* **7 (1958),** 102–113.

MARSHALL, C. E. (1964) *The Physical Chemistry and Mineralogy of Soils, Vol. I: Soil Minerals.* John Wiley, New York.

MEHRA, O. P., AND M. L. JACKSON (1960) Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. *Clays Clay Minerals, Proc. Nat. Conf.* **7 (1958)** 317–327.

STRICKLER, A. (1967) Continuous particle electrophoresis: a new analytical and preparative capability. *Separation Sci.,* **2,** 335–355.

———, A. KAPLAN, AND E. VIGH (1966) Continuous microfractionation of particle mixtures by electrophoresis. *Microchemical J.,* **10,** 529–544.